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<b>(21) International Application Number:</b> PCT/US95/06268 <b>(22) International Filing Date:</b> 17 May 1995 (17.05.95)  <b>(30) Priority Data:</b> 254,010 3 June 1994 (03.06.94) US  <b>(71) Applicant:</b> EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).  <b>(72) Inventors:</b> GEORGE, Scott, Ellery; 4005 Foxfire Lane, Kingsport, TN 37664 (US). UNDERWOOD, Vicki, Lynn; 1426 East Sevier Avenue, Kingsport, TN 37664 (US). GARBER, Dennis, Michael; 769 Bayless Road, Jonesborough, TN 37659 (US).  <b>(74) Agent:</b> THALLEMER, John, D.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		<b>(81) Designated States:</b> AU, CA, CN, JP, MX, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CLEAR PUMP HAIR SPRAY FORMULATIONS CONTAINING A SULFOPOLYESTER IN A HYDROALCOHOLIC LIQUID VEHICLE  <b>(57) Abstract</b>  This invention relates to a pump hair spray formulation containing 0.5 to 15 weight percent of a water-dispersible or water-dissipatable, linear sulfopolyester having a Tg of 40 °C to 50 °C and an inherent viscosity of 0.24 to 0.60 dl/g which contains repeat units from 20 to 26 mole percent dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole percent isophthalic acid, based on 100 mole percent dicarboxylic acid; 10 to 30 mole percent 1,4-cyclohexanedimethanol and 70 to 90 mole percent diethylene glycol, based on 100 mole percent diol; and up to 60 weight percent of an alcohol. The pump hair spray formulations are clear, have improved dry time and curl retention, and exhibit less than 20 NTU's, which is a measure of turbidity, even at alcohol concentrations of 60 weight percent.		

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CLEAR PUMP HAIR SPRAY FORMULATIONS CONTAINING A  
SULFOPOLYESTER IN A HYDROALCOHOLIC LIQUID VEHICLE

FIELD OF THE INVENTION

5           This invention relates to a pump hair spray  
formulation containing 0.5 to 15 weight percent of a  
water-dispersible or water-dissipatable, linear  
sulfopolyester having a Tg of 40°C to 50°C and an  
inherent viscosity of 0.24 to 0.60 dl/g which contains  
10 repeat units from 20 to 26 mole percent  
dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole  
percent isophthalic acid, based on 100 mole percent  
dicarboxylic acid; 10 to 30 mole percent  
1,4-cyclohexanedimethanol and 70 to 90 mole percent  
15 diethylene glycol, based on 100 mole percent diol; and  
up to 60 weight percent of an alcohol. The pump hair  
spray formulations are clear, have improved dry time and  
curl retention, and exhibit less than 20 NTU's, which is  
a measure of turbidity, even at alcohol concentrations  
20 up to 60 weight percent.

BACKGROUND OF THE INVENTION

Hair sprays provide human hair with a particular  
shape or configuration and function by applying a thin  
25 film of a resin or gum onto the hair to adhere adjacent  
hairs together so that they retain the particular shape  
or configuration at the time of application.

U.S. Pat. No. 5,164,177 discloses a hair spray  
formulation containing 2-40% of a linear polymer  
30 including at least one vinyl or acrylate monomer, a  
water-soluble electrolyte, 30-90% water, and 0-30%  
alcohol. The water-soluble electrolyte is added to  
lower the viscosity of the composition to achieve a  
higher percentage of polymer in the composition. Such  
35 formulations, however, have poor humidity resistance,  
hold and curl retention.

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U.S. Pat. No. 4,300,580 discloses hair spray formulations containing a water-dispersible or water-dissipatable linear sulfo-polyester fixative in a water/alcohol mixture. The diol component of the sulfopolyester contains at least 20 mole percent poly(ethylene glycol). Such formulations are fast drying and have good hair holding properties but possess the disadvantage of being very difficult to remove from the hair. For example, prolonged washing is required to completely remove the water-dispersible, linear polyester fixative to obtain hair with no tacky or sticky feel. U.S. Pat. No. 4,300,580 suggests adding other substances such as poly(alkylene ether) to increase the hardness and reduce the tackiness of the formulations. However, when such formulations containing a combination of the poly(alkylene glycol) and sulfopolyester are applied to hair and allowed to dry, the fixative causes a matting of the hair. Such matting hinders combing, brushing and styling of hair.

U.S. Pat. No. 5,266,303 discloses hair spray formulations containing a water-dispersible sulfopolyester having a glass transition temperature of 36°C to 40°C, a water-soluble polyvinyl lactam polymer, and water. The performance characteristics of such formulations are good. However, the drying time is too long, and the addition of alcohol, which would improve dry time, causes the formulations to become cloudy. Thus, the use of alcohol is not an option for improving the dry time of such formulations.

U.S. Pat. No. 5,158,762, discloses hair spray compositions containing a blend of a sulfopolyester and a water-soluble polymer in water. The sulfopolyester contains at least 40 mole percent 1,4-cyclohexanedimethanol. The performance characteristics of such formulations are good, however,

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the drying time is too long, and the addition of alcohol, which would improve dry time, causes the formulations to become cloudy. Thus, the use of alcohol is not an option for improving the dry time of such formulations.

U.S. Pat. No. 5,266,308, discloses aqueous hair spray compositions which contain a sulfopolyester, a water-soluble polymeric resin and a homopolymer of polyvinylpyrrolidone. The performance characteristics of such formulations are good, however, the drying time is too long, and the addition of alcohol, which would improve dry time, causes the formulations to become cloudy. Thus, the use of alcohol is not an option for improving the dry time of such formulations.

In contrast, the present inventors have unexpectedly determined that pump hair spray formulations which are clear and provide properties considered desirable for hair preparation such as fine spray patterns, fast drying times, prolonged curl retention under humid conditions, good holding power and resistance to build-up may be prepared with as much as 60 weight percent alcohol to facilitate rapid drying on the hair. The hair spray formulations of the present invention are clear and exhibit less than 20 NTU's which is a measure of turbidity. In the cosmetic field greater than 20 NTU's is characteristic of a cloudy mixture that is visible to the eye. At a 55% alcohol level, the drying time of the hair sprays of the present invention is less than half the time required by water based hair sprays.

#### SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a clear pump hair spray formulation.

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It is another object of the invention to provide a pump hair spray formulation which is not tacky, has a fast drying rate, acceptable body, consistency and exhibits improved curl retention.

5        Another object of the invention is to provide a pump hair spray formulation which is clear and has excellent storage stability and which does not clog the exit port of a pump container.

10       These and other objects are accomplished herein by a pump hair spray formulation having improved dry time and curl retention and exhibiting less than 20 NTU's as a measure of clarity which comprises:

15       (1) a sulfopolyester having a Tg of 40°C to 50°C and an inherent viscosity of 0.24 to 0.60 dl/g which consists essentially of repeat units from

20       (a) a dicarboxylic acid component consisting essentially of 20 to 26 mole percent dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole percent isophthalic acid, based on 100 mole percent dicarboxylic acid;

25       (b) a diol component consisting essentially of 10 to 30 mole percent 1,4-cyclohexanedimethanol and 70 to 90 mole percent diethylene glycol, based on 100 mole percent diol; and

30       (2) a water/alcohol liquid vehicle, provided the sulfopolyester, component (1), is present in an amount of 0.5 to 15 weight percent, based on the total weight of the pump hair spray formulation.

#### DESCRIPTION OF THE INVENTION

35       The pump hair sprays of the present invention exhibit less than 20 NTU's which is a measure of the

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turbidity of a mixture. In the cosmetic field greater than 20 NTU's is characteristic of a cloudy mixture that is visible to the eye. The clear pump hair spray formulations of this invention contain a sulfopolyester, component (1), in an amount of 0.5 to 15 weight percent, preferably 3 to 10 weight percent, and more preferably 5 to 8 weight percent, based on the total weight of the pump hair spray formulation.

The sulfopolyester, component (1), has a glass transition temperature of 40°C to 50°C and contains repeat units from a dicarboxylic acid, a diol and a difunctional sulfomonomer. The dicarboxylic acid component of the sulfopolyester contains 20 to 26 mole percent of dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole percent isophthalic acid, based on 100 mole percent dicarboxylic acid. The diol component of the sulfopolyester contains 10 to 30 mole percent 1,4-cyclohexanedimethanol and 70 to 90 mole percent diethylene glycol, based on 100 mole percent diol. The sulfopolyester has an inherent viscosity (I.V.) of 0.24 to 0.60 dl/g.

Component (2) of the pump hair spray is a liquid vehicle. The liquid vehicle may be water or a water/alcohol mixture. Distilled or deionized water are the preferred sources of water since tap water generally contains ions which may precipitate the sulfopolyester, component (1). Preferably a water/alcohol mixture is used wherein the alcohol is present in an amount less than 60 weight percent based on the weight of the pump hair spray formulation. More preferably, 45 to 55 weight percent of the pump hair spray formulation is alcohol. The alcohol provides faster drying of the formulation on hair as compared to formulations prepared with only water as the liquid vehicle. The alcohol is an aliphatic straight or branched chain monohydric

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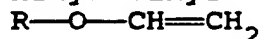
alcohol having 2 to 4 carbon atoms. Isopropanol and ethanol are the preferred alcohols.

5 In a pump hair spray formulation containing only a sulfopolyester, component (1) and a liquid vehicle, component (2), the liquid vehicle will be present in an amount of about 80 to about 99 weight percent of the pump hair spray. However, if additional ingredients are used in the pump hair spray formulation, the amount of the liquid vehicle will be proportionally reduced.

10 The pump hair spray formulations may optionally contain a water-soluble polymer or resin, component (3). The water-soluble polymer must be soluble or dispersible in liquid vehicle, component (2). The term "water-soluble" refers to any material that has  
15 solubility of at least 1 gram per 100 grams of water, i.e. 1%, preferably a solubility of at least 5% by weight. Conversely, the term "water-insoluble" refers to substances that are insoluble at a level of less than 1 gram per 100 grams of water, i.e., less than 1% by  
20 weight. Solubility or dispersibility is determined at ambient conditions (e.g., a temperature of about 25°C and atmospheric pressure).

Water-soluble polymers useful in the formulations of the present invention are homopolymers or copolymers  
25 that can be rendered dispersible or soluble in aqueous or water/alcohol mixtures. The water-soluble polymer is a synthetic, linear, homopolymer or random copolymer including at least one, and preferably two or more, vinyl or acrylate monomers of the following group:

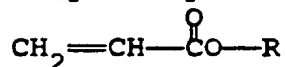
30 Alkyl vinyl ethers



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Alkyl Acrylates

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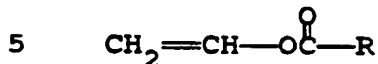


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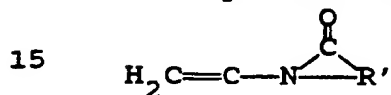


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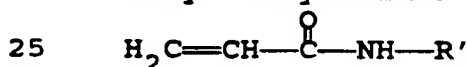
## Vinyl esters



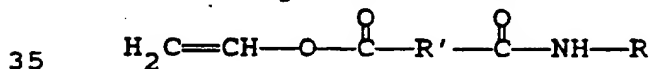
## 10 N-vinyl lactams



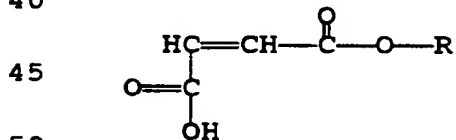
## 20 Alkyl acrylamides



## 30 Half vinyl esters/half amides

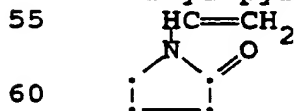


## 40 Half esters of maleic anhydride



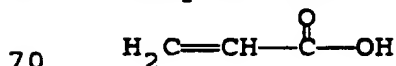
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## Vinyl pyrrolidone

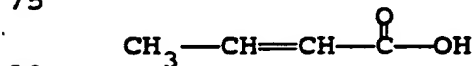


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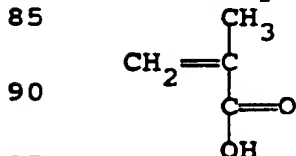
## 65 Acrylic acid



## 75 Crotonic Acid



## 85 Methacrylic acid



95

In the above formulas, R is a C<sub>1</sub> to C<sub>10</sub> alkyl and R' is a C<sub>1</sub> to C<sub>10</sub> alkylene. Preferred monomers for use in the water-soluble polymers are acrylic acid, vinyl

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pyrrolidone, vinyl acetate, crotonic acid, methacrylic acid or a combination thereof. Examples of preferred copolymers are the mono ethyl, isopropyl or n-butyl esters of poly(methyl vinyl ether/maleic acid);

5 poly(vinyl pyrrolidone/vinyl acetate, poly(vinyl pyrrolidone/ethyl methacrylate/methacrylic acid), poly(ethyl acrylate/acrylic acid/N-t-butyl acrylamide), and poly(vinyl acetate/crotonic acid).

Other suitable classes of water-soluble polymers  
10 include anionic, nonionic, amphoteric and cationic polymers. Specific polymers include polyvinylpyrrolidone (PVP), copolymers of PVP and methylmethacrylate, copolymers of PVP and vinyl acetate (VA), polyvinyl alcohol (PVA), copolymers of PVA  
15 and crotonic acid, copolymers of PVA and maleic anhydride, hydroxypropyl cellulose, hydroxypropyl guar gum, sodium polystyrene sulfonate, PVP/ethylmethacrylate/methacrylic acid terpolymer and octylacrylamide/acrylate/butylaminoethyl methacrylate  
20 copolymers, and mixtures. A preferred vinyl polymer or copolymer contains at least 50 mole percent of the residues of n-vinyl lactam monomer such as N-vinylpyrrolidinone.

With certain of the acidic water-soluble polymers,  
25 it may be necessary to neutralize some acidic groups to promote solubility/dispersibility, e.g., PVA/crotonic acid. Neutralization and increased solubilization are accomplished with one or more inorganic bases such as sodium hydroxide, potassium hydroxide, ammonium  
30 hydroxide and/or ammonium carbonate. Among stable organic bases are the water soluble bases such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-methyl-2-amino-1-propanol (AMP), monoamino glycols, and the like, which help  
35 solubilize the polymer in water solutions. The level of

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neutralization required for solubilization varies for each polymer. All of the above-described acidic polymers become soluble in water and hydroalcoholic solutions at 100% neutralization, and all described levels of water/alcohol solutions. The pH of these solutions usually ranges from 9 to 12. The lowest neutralization level needed to render the polymer water soluble or dispersible depends on the kind of polymer, and the amount of alcohol and water. For instance, for poly(methyl vinyl ether/maleic acid) in water the lowest neutralization level is about 40% with sodium hydroxide and AMP; for poly(ethyl acrylate/acrylic acid/N-t-butyl acrylamide) the lowest neutralization level is about 75% with AMP and 65% with sodium hydroxide. At these neutralization levels, the pH of the solutions range from about 5 to about 7. A slightly acidic or neutral pH such as this is preferred, however, the pH of the formulations of the present invention can vary from about 4 to about 9. Saponification of the ester linkages may occur under alkaline conditions.

The water-soluble polymers may be prepared according to known procedures wherein, for example, a N-vinyl lactam is polymerized, optionally in the presence of one or more other vinyl monomers such as those described above. The N-vinylpyrrolidinone/vinyl acetate copolymers supplied by BASF under the trademark LUVISKOL VA are typical of the water-soluble polymers which may be used in the pump hair spray formulations of the present invention. The preferred water-soluble polymers comprise homopolymers of N-vinyl-2-pyrrolidinone and copolymers of N-vinyl-2-pyrrolidinone and up to 50 mole percent vinyl acetate having weight average molecular weights in the range of about 1000 to 100,000. The water-soluble polymers are used at a level of from about 0.5% to about

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10% by weight, generally about 1% to about 5% by weight, and preferably from 2% to 4% by weight of the total formulation. The weight average molecular weight of the polymers is not critical but is generally in the range  
5 from about 1,000 to 2,000,000.

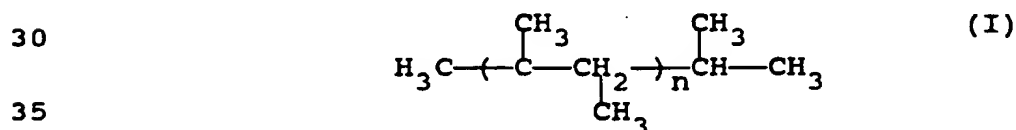
The pump formulations also can contain a variety of other nonessential, optional components suitable for rendering such formulations more acceptable. Such conventional optional ingredients are well known to  
10 those skilled in the art, e.g., other emulsifiers such as anionics (e.g., sodium alkyl sulfate); preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinylurea; cationic  
emulsifiers/conditioners such as cetyl trimethyl  
15 ammonium chloride, stearyl-dimethyl benzyl ammonium chloride, and di(partially-hydrogenated tallow)  
dimethylammonium chloride; thickeners and viscosity modifiers such as diethanolamide of a long chain fatty acid, fatty alcohols (i.e., cetearyl alcohol), sodium  
20 chloride, sodium sulfate, and ethyl alcohol; pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine; coloring agents such as any of the FD&C or D&C dyes; hair oxidizing  
(bleaching) agents such as hydrogen peroxide, perborate  
25 salts and persulfate salts; hair reducing agents such as thioglycolates; perfume oils; chelating agents such as ethylenediaminetetraacetic acid; and among many other  
agents, polymer plasticizing agents such as glycerin and propylene glycol. These optional materials are  
30 generally used individually at a level of from about 0.001% to about 19%, preferably from 0.01% to 5% by weight of the total formulation. It is important to note that the use of cationic emulsifiers in amounts of  
greater than 1% may precipitate the sulfopolyester,  
35 component (1).

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The pump hair-spray formulation of the present invention may also include from about 0.01% to 10%, preferably, 0.1% to 2% by weight of a non-volatile silicone compound or other conditioning agent(s), preferably a water-insoluble, emulsifiable conditioning agent. The preferred non-volatile silicone compound is a polydimethylsiloxane compound, such as a mixture of a low molecular weight polydimethylsiloxane fluid and a higher molecular weight polydimethylsiloxane gum. The non-volatile polydimethylsiloxane compound is added to the formulation of the present invention in an amount sufficient to provide improved combing and improved feel (softness) to the hair after shampooing.

Another particularly suitable conditioning agent that can be included in the formulation of the present invention is a volatile hydrocarbon, such as a hydrocarbon including from about 10 to about 30 carbon atoms, that has sufficient volatility to slowly volatilize from the hair after application of the pump hair spray formulation. The volatile hydrocarbons provide essentially the same benefits as the silicone conditioning agents.

The preferred volatile hydrocarbon compound is an aliphatic hydrocarbon including from about 12 to about 24 carbon atoms, and having a boiling point in the range of from about 100° C to about 300°C. Exemplary volatile hydrocarbons are depicted in general structural formula (I), wherein n ranges from 2 to 5,



Examples of volatile hydrocarbons useful in the pump hair spray formulation of the present invention are the commercially-available compounds PERMETHYL 99A and

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PERMETHYL 101A, corresponding to compounds of general structure (I) wherein n is 2 and 3, respectively, available from Permethyl Corporation, Frazer, Pa. A volatile hydrocarbon compound is useful in the formulation of the present invention either alone, in combination with another volatile hydrocarbon, or in combination with a volatile silicone.

Examples of other suitable water-insoluble conditioning agents that can be incorporated into the hair spray formulations of the present invention include the following: polysiloxane polyether copolymers; polysiloxane polydimethyl dimethylammonium acetate copolymers; acetylated lanolin alcohols; lauryl dimethylamine oxide; a lanolin-derived extract of sterol on sterol esters; lanolin alcohol concentrate; an isopropyl ester of lanolin fatty acids; sulfur rich amino acid concentrates; isopropyl ester of lanolin fatty acids; oleyl alcohol; stearyl alcohol; stearamidopropyl dimethyl myristyl acetate; a polyol fatty acid; a fatty amido amine; guar hydroxypropyltrimonium chloride; cetyl/stearyl alcohol; keratin protein derivatives; isostearamidopropyl dimethylamine; stearamidopropyl dimethylamine; an aminofunctional silicone; isopropyl ester of lanolic acids, ethoxylated (30) castor oil; acetylated lanolin alcohol, fatty alcohol fraction of lanolin, a mineral oil and lanolin alcohol mixture; high molecular weight esters of lanolin; vinylpyrrolidone/dimethylaminoethylmethacrylate copolymer, 5 mole ethylene oxide adduct of soya sterol; 10 mole ethylene oxide adduct of soya sterol; stearic acid ester of ethoxylated (20 mole) methyl glucoside; sodium salt of polyhydroxycarboxylic acid; hydroxylated lanolin; cocamidopropyl dimethylamine lactat ; cocamidopropyl dimethylamine propionate; cocamidopropyl

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morpholine lactate; isostearamidopropyl dimethylamine lactate; isostearamidopropyl morpholine lactate; oleamidopropyl dimethylamine lactate; linoleamidopropyl dimethylamine lactate; stearamidopropyl dimethylamine lactate, ethylene glycol monostearate and propylene glycol mixture; stearamidopropyl dimethylamine lactate; acetamide MEA; lactamide MEA; stearamide MEA; behenalkonium chloride; behenyl trimethyl ammonium methosulfate and cetearyl alcohol mixture; cetearyl alcohol; tallow imidazolinum methoxulfate, stearyl trimonium methosulfate; mixed ethoxylated and propoxylated long chain alcohols; stearamidopropyl dimethylamine lactate, polonitamine oxide; oleamine oxide, stearamide oxide; soya ethyldimonium ethosulfate; ricinoleamidopropyl ethyldimonium ethosulfate; N-(3-isostearamidopropyl)-N,N-dimethyl amino glycolate; N-(3-isostearamidopropyl)-N,N-dimethyl amino gluconate; hydrolyzed animal keratin; ethyl hydrolyzed animal keratin; stearamidoethyl diethylamine; cocamidopropyl dimethylamine; lauramidopropyl dimethylamine, oleamidopropyl dimethylamine; palmitamidopropyl dimethylamine; stearamidopropyl dimethylamine lactate; avocado oil; sweet almond oil, grape seed oil; jojoba oil; apricot kernel oil; sesame oil; hydrid safflower oil; wheat germ oil; cocamidoamine lactate; ricinoleamido amine lactate; stearamido amine lactate; stearamido morpholine lactate; isostearamido amine lactate; isostearamido morpholine lactate; wheat germamido dimethylamine lactate; wheat germamidopropyl dimethylamine oxide; disodium isostearamido MEA sulfosuccinate; disodium oleamide PEG-2 sulfosuccinate; disodium oleamide MEA sulfosuccinate; disodium ricinoleyl MEA sulfosuccinate; disodium wheat germamido MEA sulfosuccinate; disodium wheat germamido PEG-2 sulfosuccinat ; st aramido amine; stearamido morpholine;

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isostearamido amine; isostearamido morpholine;  
polyethylene glycol (400) mono and distearates;  
synthetic calcium silicate; isostearic alkanolamide;  
ethyl esters of hydrolyzed animal protein; blend of  
5 cetyl and stearyl alcohols with ethoxylated cetyl or  
stearyl alcohols; amido amines; polyamido amines;  
propoxylated (1-20 moles) lanolin alcohols;  
isostearamide DEA; and hydrolyzed collagen protein.  
Water-insoluble cationic conditioning agents in amounts  
10 of less than about 1% may also be used. The use of  
water-insoluble cationic conditioning agents in amounts  
of greater than 1% may precipitate the sulfopolyester,  
component (1).

The aqueous formulations of the present invention  
15 also can contain the conventional hair spray adjuvants  
in amounts which generally range from about 0.01 to 2%  
by weight and preferably 0.1% to 1% by weight. Among  
the additives which can be used are plasticizers such as  
glycols, phthalate esters and glycerine; silicones;  
20 emollients; lubricants and penetrants such as various  
lanolin compounds; protein hydrolysates and other  
protein derivatives; ethylene adducts and  
polyoxyethylene cholesterol; dyes, tints and other  
colorants; and perfumes.

25 Other conventional additives such as preservatives,  
fragrances, antifoaming agents, hair conditioners,  
plasticizers, etc. may be added in such quantities as  
desired, up to about 5.0% by weight of the total  
formulation. Although the film-forming formulations  
30 described herein are particularly useful as pump hair  
sprays for the grooming of hair, it is possible that the  
formulations, with or without modification, may be used  
in other types of personal care products.

Suitable plasticizers include: Dimethicone Copolyol  
35 (Dow Corning 190) at 0.01-0.02%, PEG-6 Capric/Caprylic



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Glyceride (Softigen 767) at 0.5-2.0%, Diacetin at 1.0-2.0, Lauramide DEA (Monamid 716) at 0.1-1.0%, Phenyl Trimethicone (Abil AV 20-1000) at 0.1-0.2%, propylene glycol at 1.0-5.0%, dipropylene glycol at 1.0-5.0%.

5       The materials and testing procedures used for the results shown herein are as follows:

          LUVISKOL VA 73W PVP/VA (CTFA Adopted Name: PVP/VA Copolymer), available from BASF, is a water-soluble vinyl copolymer of 70 mole percent of  
10   N-vinyl-2-pyrrolidinone and 30 mole percent of vinyl acetate (50% solid).

          SDA-40C is ethanol that has been diluted with ethyl acetate, and is available from Eastman Chemical Company.

          Glass transition temperature was determined using a  
15   differential scanning calorimeter (DSC).

          Inherent viscosity (I.V.) was measured at 23°C using 0.50 grams of polymer per 100 ml of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

20       Turbidity was measured in NTU's using a model DRT-100B Turbidimeter.

          The invention will be further illustrated by a consideration of the following examples, which are intended to be exemplary of the invention. All parts  
25   and percentages in the examples are on a weight basis unless otherwise stated.

#### EXAMPLE I

Preparation of water-dispersible Sulfopolyesters A-D.

30       A round bottom flask equipped with ground-glass head, an agitator shaft, nitrogen inlet and a side arm was charged with isophthalic acid, dimethyl-5-sodiosulfoisophthalate (SIP), diethylene glycol (DEG), and 1,4-cyclohexanedimethanol (CHDM), in the mole  
35   percents as set forth below. For comparison purposes,

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Table I summarizes critical values for each sulfopolyester. A catalyst was added and the flask was immersed in a Belmont bath at 200°C for one hour under a nitrogen sweep. The temperature of the bath was  
5 increased to 230°C for one hour. The temperature of the bath was increased to 280°C and the flask was heated for 45 minutes under reduced pressure of 0.5 to 0.1 mm of Hg. The flask was allowed to cool to room temperature and the sulfopolyester was removed from the flask. Each  
10 sulfopolyester was extruded and pelletized.

More specifically, the composition of each sulfopolyester was as follows:

Sulfopolyester A was prepared with 24.4 mole percent dimethyl-5-sodiosulfoisophthalate and 75.6 mole percent  
15 isophthalic acid, and 25.3 mole percent 1,4-cyclohexanedimethanol and 74.7 mole percent diethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol. Sulfopolyester A has a Tg of 47°C and an I.V. of  
20 0.32 dl/g.

Sulfopolyester B was prepared with 23.1 mole percent dimethyl-5-sodiosulfoisophthalate and 76.9 mole percent isophthalic acid, and 23.5 mole percent  
25 1,4-cyclohexanedimethanol and 76.5 mole percent diethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol. Sulfopolyester B has a Tg of 46°C and an I.V. of 0.26 dl/g.

Sulfopolyester C was prepared with 18.0 mole percent dimethyl-5-sodiosulfoisophthalate and 82.0 mole percent  
30 isophthalic acid, and 46.0 mole percent 1,4-cyclohexanedimethanol and 54.0 mole percent diethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

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Sulfopolyester C has a Tg of 55°C and an I.V. of 0.33 dl/g.

Sulfopolyester D was prepared with 11.0 mole percent dimethyl-5-sodiosulfoisophthalate and 89.0 mole percent isophthalic acid, and 22.0 mole percent 1,4-cyclohexanedimethanol and 78.0 mole percent diethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

Sulfopolyester D has a Tg of 38°C and an I.V. of 0.36 dl/g.

TABLE I

Summary of Sulfopolyester Compositions:

	<u>Sulfopolyester</u>	<u>SIP</u>	<u>CHDM</u>	<u>I.V.</u>	<u>Tg</u>
15	A	24.4	25.3	0.32	47°C
	B	23.1	23.5	0.26	46°C
	C	18.0	46.0	0.33	55°C
	D	11.0	22.0	0.36	38°C

## EXAMPLE II

Preparation of pump hair spray formulations using Sulfopolyesters A-D prepared in Example I.

Ten grams of each of the sulfopolyesters were dispersed in distilled water by heating and stirring until a temperature of 75° to 85°C was reached. After cooling to 40°C any water lost during heating was replaced and in some cases a water-soluble polymer consisting of 70 mole percent of N-vinyl-2-pyrrolidinone and 30 mole percent of vinyl acetate (50% solids) was added. In some cases ethanol, as SDA 40C, was added. The mixtures were vacuum filtered through a coarse center glass filter. A preservative, 1-(hydroxymethyl)-5,5-dimethyl hydantoin, 0.2 grams, was added.

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The mixtures were poured into a glass cuvette which was placed in the Turbidimeter. The turbidity results are listed in Tables II and III.

TABLE II  
Turbidity Results (NTU's)  
Using Sulfopolyesters (A-D)

Example		A	B	C	D
5	10% Sulfopoly 0% EtOH	13	11	36	80
10	10% Sulfopoly 20% EtOH	9	9	25	56
	10% Sulfopoly 30% EtOH	8	8	27	48
15	10% Sulfopoly 35% EtOH	8	8	25	47
	10% Sulfopoly 40% EtOH	9	8	65	43
20	10% Sulfopoly 45% EtOH	10	9	53	54
	10% Sulfopoly 50% EtOH	9	9	66	95
25	10% Sulfopoly 55% EtOH	13	17	886	220
30					

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TABLE III  
Turbidity Results (NTU's)  
Using Sulfopolyesters (A-D)

Example	A	B	C	D
5				
7% Sulfopoly 3% PVP/VA 0% EtOH	15	11	30	71
10				
7% Sulfopoly 3% PVP/VA 20% EtOH	7	8	27	60
15				
7% Sulfopoly 3% PVP/VA 30% EtOH	6	6	21	44
20				
7% Sulfopoly 3% PVP/VA 35% EtOH	6	6	18	42
25				
7% Sulfopoly 3% PVP/VA 40% EtOH	6	6	52	39
30				
7% Sulfopoly 3% PVP/VA 45% EtOH	6	7	46	48
35				
7% Sulfopoly 3% PVP/VA 50% EtOH	6	7	61	85
40				
7% Sulfopoly 3% PVP/VA 55% EtOH	9	19	911	99

The results in Tables II and III clearly indicate that pump hair sprays prepared with Sulfopolyesters A and B, which meet the criteria of the present invention, result in clear hair sprays even at 55% alcohol. The hair sprays prepared with Sulfopolyesters A and B exhibit significantly less than 20 NTU's which is a measure of turbidity. Greater than 20 NTU's is characteristic of a cloudy mixture. Moreover, the presence of a water-soluble polymer in the formulations

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of the present invention does not deleteriously effect the clarity of the pump hair spray formulations. In contrast, the addition of alcohol to hair spray formulations prepared with Sulfopolyester C or D, commonly known as Eastman AQ 55 and Eastman AQ 38, respectively, result in cloudy hair spray formulations with as little as 10% alcohol for Eastman AQ 38.

Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious modifications are within the full intended scope of the appended claims.

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## WHAT IS CLAIMED IS

1. A clear pump hair spray formulation having improved dry time comprising:

(1) a sulfopolyester having a Tg of 40°C to 50°C and an inherent viscosity of 0.24 to 0.60 dl/g which consists essentially of repeat units from

(a) a dicarboxylic acid component consisting essentially of 20 to 26 mole percent dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole percent isophthalic acid, based on 100 mole percent dicarboxylic acid;

(b) a diol component consisting essentially of 10 to 30 mole percent 1,4-cyclohexanedimethanol and 70 to 90 mole percent diethylene glycol, based on 100 mole percent diol; and

(2) a water/alcohol liquid vehicle, provided the sulfopolyester, component (1), is present in an amount of 0.5 to 15 weight percent, based on the total weight of the pump hair spray formulation.

2. A clear pump hair spray formulation exhibiting less than 20 NTU's and having improved dry time comprising:

(1) 0.5 to 15 weight percent of a sulfopolyester having a Tg of 40°C to 50°C and an inherent viscosity of 0.24 to 0.60 dl/g which consists essentially of repeat units from

(a) a dicarboxylic acid component consisting essentially of 20 to 26 mole percent dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole percent isophthalic acid, based on 100 mole percent dicarboxylic acid;

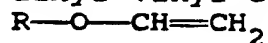
- 22 -

- (b) a diol component consisting essentially of 10 to 30 mole percent 1,4-cyclohexanedimethanol and 70 to 90 mole percent diethylene glycol, based on 100 mole percent diol; and
- (2) a water/alcohol liquid vehicle comprising 25 to 69.5 percent water and 30 to 60 percent alcohol, based on the total weight of the pump hair spray formulation.
3. A clear pump hair spray formulation exhibiting less than 20 NTU's and having improved dry time comprising:
- (1) 3 to 10 weight percent of a sulfopolyester having a Tg of 40°C to 50°C and an inherent viscosity of 0.24 to 0.60 dl/g which consists essentially of repeat units from
- (a) a dicarboxylic acid component consisting essentially of 20 to 26 mole percent dimethyl-5-sodiosulfoisophthalate and 74 to 80 mole percent isophthalic acid, based on 100 mole percent dicarboxylic acid;
- (b) a diol component consisting essentially of 10 to 30 mole percent 1,4-cyclohexanedimethanol and 70 to 90 mole percent diethylene glycol, based on 100 mole percent diol;
- (2) a water/alcohol liquid vehicle comprising 20 to 61.5 percent water and 35 to 60 percent alcohol, based on the total weight of the pump hair spray formulation; and
- (3) 0.5 to 10 weight percent based on the weight of components (1), (2), and (3) of a water-soluble polymer, which is prepared from at least one vinyl or acrylate monomer selected from the group consisting of



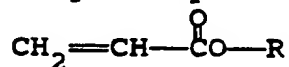
- 23 -

alkyl vinyl ethers



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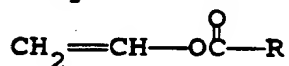
alkyl acrylates



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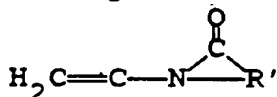
vinyl esters



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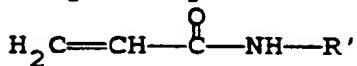
N-vinyl lactams



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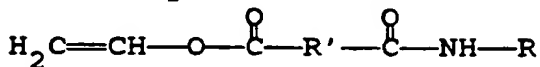
alkyl acrylamides



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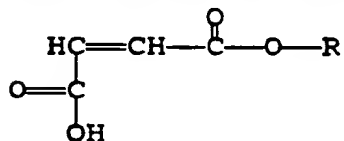
half vinyl esters/half amides



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55

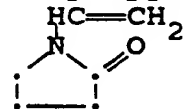
half esters of maleic anhydride



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vinyl pyrrolidone

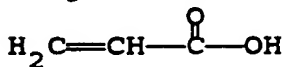


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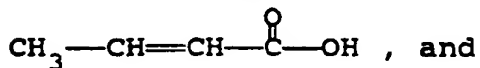
acrylic acid



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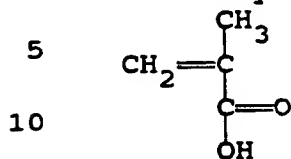
crotonic acid



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- 24 -

methacrylic acid



15 wherein R is a C<sub>1</sub> to C<sub>10</sub> alkyl and R' is a C<sub>1</sub> to C<sub>10</sub> alkylene.

4. The pump hair spray formulation of Claim 3 wherein the water-soluble polymer, component (3), is selected from the group consisting of polyvinyl pyrrolidone, polyvinyl caprolactam, polyvinyl acetate, polyacrylates, methacrylates, and copolymers and terpolymers of such monomers.

25 5. The pump hair spray formulation of Claim 4 wherein the water-soluble polymer is a polyvinyl lactam polymer containing at least 50 mole percent of residues of N-vinyl lactams of the formula



wherein n is 3 or 4.

40

6. The pump hair spray formulation of Claim 1 wherein the alcohol is present in an amount less than 60 percent based on the weight of the pump hair spray formulation.

45 7. The pump hair spray formulation of Claim 1 wherein the alcohol is present in an amount of 30 to 60 percent based on the weight of the pump hair spray formulation.

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8. The pump hair spray formulation of Claim 7 which contains 35 to 55 weight percent alcohol.

9. The pump hair spray formulation of Claim 8 which  
5 contains 45 to 55 weight percent alcohol.

10. The pump hair spray formulation of Claim 1 wherein the alcohol is an aliphatic straight or branched chain monohydric alcohol having 2 to 4 carbon atoms.

10

11. The pump hair spray formulation of Claim 10 wherein the alcohol is selected from the group consisting of isopropanol and ethanol.

12. The pump hair spray formulation of Claim 11 wherein  
15 the alcohol is ethanol.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/06268

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 00105 (EASTMAN) 5 January 1995 see claims; example VIII ---	1-12
A	US,A,4 300 580 (O'NEIL ET AL) 17 November 1981 cited in the application see column 4, line 27 - line 34; example 3 ---	1
A	US,A,5 158 762 (PIERCE) 27 October 1992 cited in the application see claims -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
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- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

16 October 1995

Date of mailing of the international search report

31. 10. 95

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Loiselet-Taisne, S

**INTERNATIONAL SEARCH REPORT**

Intern: al Application No

**PCT/US 95/06268**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A-4300580	17-11-81	NONE	
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		WO-A- 9317658	16-09-93

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